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(54) Transparent diamond films and method for making

Durchsichtige Diamantschichten und Verfahren zu ihrer Herstellung

Films de diamant transparents et méthode pour leur fabrication

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EP 0 676 484 B1

Description

[0001] The present invention relates to vapor deposited transparent polycrystalline diamond films. More particularly, the present invention relates the method of introducing a particular mixture of hydrogen and methane into a heated reaction zone adjacent to a substrate such as molybdenum, to effect polycrystalline diamond film deposition.

[0002] As taught by Spear, Diamond-Ceramic Coating Of The Future, Journal of American Ceramics Society, 72[2]171-91 (1989), the growth of single-crystal films of diamond is critical to many electronic and optical applications, but it is a feat that has not been achieved except for homoepitaxial growth on diamond substrates. There is reported by Peter K. Backmann, et al in the May 15, 1989, edition of Chemical and Engineering News, on page 38, that vapor deposited diamond heat sinks have been developed using plasma jet deposition to produce polycrystalline material up to 4 x 6 x 1 millimeter.

[0003] In Japanese patent 85,141,697, it is reported that free-standing diamond films have been found useful as diaphragms for speakers. S. Kawachi et al, Japanese patent 85(60)-127,292, reports that 10 µm (micron) diamond films have been deposited on a graphite substrate. K. Fujii, et al, Japanese patent 85(60)-186,500 teaches that a 6.5 µm (micron) thick transparent film can be produced on a substrate using a methane-hydrogen mixture.

[0004] SPIE Vol.1146 Diamond Optics II (1989) pages 192-200 "Optical Transmission and Reflection of Free-standing Filament Assisted CVD diamond Films" discloses room-temperature optical studies on ~10µm free-standing diamond films grown on Si (100) substrates by hot-filament-assisted CVD from a methane/hydrogen mixture.

[0005] Although various procedures have been developed to make vapor deposited polycrystalline diamond film, it would be desirable to provide glazing materials in the form of free-standing polycrystalline transparent diamond films having thicknesses of from 50 to 5000 µm (microns) with lateral dimensions exceeding 10 millimeters.

Summary of the Invention

[0006] The present invention is based on the discovery that vapor deposited transparent polycrystalline diamond film can be made at thicknesses greater than 50 µm (microns) by passing a particular hydrogen-methane mixture through a filament heated reaction zone adjacent to a suitable substrate, such as a molybdenum substrate, where the hydrogen-methane mixture introduced into the reaction zone has from about 1.5 to about 2 volume percent of methane, based on the total volume of hydrogen and methane. Surprisingly, a transparent non-adherent polycrystalline diamond film having an optical absorbance of 2.1 cm^{-1} to 32 cm^{-1} can be formed at a growth rate of about 0.4 to 1.0 µm (microns) per hour. Thicknesses of at least 50 µm (microns), and as high as 5000 µm (microns) or more, can be made having lateral dimensions exceeding 25 centimeters.

Statement of the Invention

[0007] There is provided by the present invention, a continuous free-standing, substantially transparent, polycrystalline diamond film having a thickness of at least 50 µm (microns) comprising (A) substantially vertical columnar diamond crystals having an average diameter of from about 20 to about 200 µm (microns) and a <110> orientation perpendicular to the base and up to 10,000 parts per million of chemically combined hydrogen which is sufficient to substantially saturate dangling carbon bonds at diamond crystal grain boundaries, carbon dislocations, and carbon vacancies and (B) diamond crystal grain boundaries separating the columnar diamond crystals of (A) where the diamond crystal grain boundaries have a 70°-90° orientation to the diamond crystal base.

[0008] In another aspect of the present invention, there is provided a method of growing a non-adherent substantially transparent polycrystalline diamond film on a substrate which comprises, passing a hydrogen-methane mixture through a heated reaction zone at a temperature of about 600° to about 1000°C and at a pressure from about 400-3199 Pa (3 to about 24 torr) which is sufficient to generate active carbon-hydrogen species in the heated reaction zone maintained at a distance of from about 0.3 to about 1 centimeter from the surface of the substrate, where the hydrogen-methane mixture introduced into the heated reaction zone has from 1.5 to about 2 volume percent of methane, based on the total volume of hydrogen and methane.

[0009] A typical apparatus which can be used to form the transparent polycrystalline diamond film of the present invention is shown by Figure 1. Figure 1 shows a quartz bell jar having a metal flange which rests on a base. Inside the quartz bell jar, there is shown a support structure for a filament and several adjacent substrate sections.

[0010] More particularly, there is shown a quartz bell jar at 10 which can be 50.8-76.2 cm (20"-30") tall and about 10.16-15.24 cm (4"-6") wide having a metal collar at its base at 11 and a gas inlet at the top at 12. The metal collar portion rests on a rubber seal at 13 which can be Neoprene (RTM) rubber. The rubber seal is supported by a metal base, such as steel base structure at 14 which has a vacuum opening at 15.

[0011] Inside the quartz bell jar there is shown a supporting stand at 16 for an extension at 17 for holding several substrate structures, such as molybdenum at 18 and 19 and a filament at 20. The filament is secured by a screw at 21 to a metal plug at 22 which passes through a quartz insulating collar at 23 which is supported by an

extension at 24. Electrical contacts are shown from the plug at 25 to a stud at 26 which is insulated from the metal base at 27.

[0012] Reference also is made to Figure 2, showing a top view through an optical microscope of 10 to 200 µm (micron) columnar diamond crystals of the polycrystalline diamond film of the present invention separated by atomic grain boundaries.

[0013] A further reference to the polycrystalline diamond film of the present invention is shown by Figure 3 and Figure 3A. A side view of the polycrystalline diamond film in cross section,and a detail at 3A further illustrates the substantially transparent columns of diamond crystals having a <110> orientation perpendicular to the base. Grain boundaries between adjacent diamond crystals having hydrogen atoms saturating dangling carbon bonds are shown at 40 and in detail at 41, where at least 50% of the carbon atoms are believed to be tetrahedrally bonded based on Raman spectroscopy, infrared and X-ray analysis.

[0014] A detailed discussion of Miller Indices describing crystal planes of atoms differentiating between <010>, <110> and <111> orientation is shown on pages 65-69 In Elements of Material Science, Second Edition, 1964, by Lawrence H. VanVlack of Addison-Wisley Publishing Company, Reading, Massachusetts which is incorporated herein by reference.

[0015] A detailed discussion on chemical bonding and structure discussing the hybridization theory and molecular geometry with respect to tetrahedral bonding of carbon atoms with hydrogen is shown by Ernest Griswold, Chemical Bonding and Structure, pages 55-102, 1968, Raytheon Education Company, which is incorporated herein by reference.

[0016] The following shows that dissociation of hydrogen and methane on a heated tungsten filament in accordance with the practice of the method of the present invention.

$$CH_4(g)+\square=CH_4(ad) \quad (1)$$

$$CH_4(ad)=CH_3(ad)+H\ (ad) \quad (2)$$

$$CH_3(ad)=CH_2(ad)+H(ad) \quad (3)$$

$$CH_2(ad)=CH\ (ad)+H\ (ad) \quad (4)$$

$$CH(ad)=C(ad)+H(ad) \quad (5)$$

$$C(ad)=C(g)+\square \quad (6)$$

$$CH(ad)=CH(g)+\square \quad (7)$$

$$CH_2(ad)=CH2(g)+\square \quad (8)$$

$$CH_3(ad)=CH_3(g)+\square \quad (9)$$

$$C(ad)=\square+C(\text{in filament}) \quad (10)$$

$$H_2(g)+2\square=2H(ad) \quad (11)$$

$$H(ad)=H(g)+\square \quad (12)$$

$\square$ =vacant surface site
(g)=gaseous species
(ad)=species absorbed on surface.

[0017] The above mechanism is one possible explanation as to how the transparent diamond film grows on the substrate.

[0018] As described by Ch. Wild et al. in the First Proceedings For International ECS Symposium on Diamond and Diamond-Like Films, Los Angeles, May 7-12, 1989 for "Optical and Structural Characterization of CVD Diamond", which is incorporated herein by reference, infrared and Raman spectroscopy as well as X-ray diffraction have been used to investigate polycrystalline diamond films prepared by the method of the present invention. The absorption spectrum of a 400 µm (micron) thick free-standing diamond wafer established that the film had a hydrogen concentration of about 5000 part per million. Raman spectroscopy was used to establish that the observed polycrystalline film was significantly different from graphite, since it contained a significant level of tetrahydral carbon atoms. X-ray diffraction measurements revealed that the polycrystalline film made in accordance with the practice of the present invention had a preferential alignment of the <110> planes perpendicular to the growth direction and indicated that the diamond crystal grain boundaries had a 70°-90° orientation to the base.

[0019] The polycrystalline diamond films made in accordance with the practice of the present invention can be used in a variety of glazing applications as well as heat sinks or semiconductors.

[0020] In order that those skilled in the art will be better able to practice the present invention, the following example is given by way of illustration and not by way of limitation.

Example

[0021] A mixture of 1.75 volume % of methane and 98.25 volume % of hydrogen, measured under atmospheric conditions, was introduced into a reaction vessel as shown by Figure 1. A gas flow rate of about 400 cubic centimeters per minute was maintained. There was used two 3.2x0.6x22.9 cm (1 1/4" x 1/4" x 9") molybdenum substrates and a 24.1 cm (9 1/2") #218 tungsten filament having a diameter of 0.76 mm (.030"). The tungsten filament was maintained at a temperature between about 2020 to 2040°C. A separation of about 7-8 millimeters was maintained between the filament and the molybdenum substrate during the deposition which lasted approximately 30 days. The substrate temperature was estimated at about 800°C during the deposition period.

[0022] At the termination of the 30 day deposition period, the apparatus was allowed to cool to room temperature. Transparent polycrystalline diamond films having thicknesses of about 500 µm (microns) and lateral dimensions equivalent to the substrates separated from the substrate during the cooling period.

[0023] The diamond films were found to be of good crystalline quality as shown by Raman spectra having an intense peak at 1332 cm^{-1}. The diamond films were also found to have the characteristic two phonon adsorption of material diamond in the range of 1600-2650 cm^{-1} by infrared spectroscopy.

[0024] Although the above example is directed to only a few of the very many variables which can be used in the practice of the method of the present invention to make the polycrystalline diamond films, it should be understood that a much broader variety of conditions, apparatus arrangements and materials can be used as set forth in the description preceding this example.

Claims

1. A transparent or substantially transparent polycrystalline diamond film having a thickness of at least about 50 µm (microns).

2. A transparent or substantially transparent diamond film in accordance with Claim 1, wherein the diamond film has a thickness between about 200 µm (microns) and about 500 µm (microns).

3. A transparent or substantially transparent diamond film in accordance with Claim 1 or Claim 2 wherein the diamond film comprises substantially vertical columnar diamond crystals having a preferred [110] orientation perpendicular to the base of the film.

4. A substantially transparent diamond film in accordance with any preceding claim having up to 10,000 ppm of chemically combined hydrogen.

5. A substantially transparent diamond film in accordance with any preceding claim, having diamond grain boundaries separating the columnar diamond crystals where said boundaries have between a 70° to a 90° orientation to the base of the film.

6. A method of growing a non-adherent substantially transparent polycrystalline diamond film on a substrate which comprises passing a hydrogen-methane mixture through a heated zone at a temperature of about 600°C to about 1000°C at a pressure of about 400 to 3199 Pa (3 to about 24 torr) which is sufficient to generate active carbon-hydrogen species in the heated zone maintained at a distance of from about 0.3 to about 1 centimeter on the surface of the substrate, where the hydrogen-methane mixture introduced into the heated zone has from about 1.5 to about 2 volume% of methane based on the total volume of hydrogen and methane.

7. A method in accordance with claim 6, where the substrate is a molybdenum substrate.

Patentansprüche

1. Transparenter oder im wesentlichen transparenter polykristalliner Diamantfilm mit einer Dicke von mindestens etwa 50 µm.

2. Transparenter oder im wesentlichen transparenter Diamantfilm gemäß Anspruch 1, worin der Diamantfilm eine Dicke zwischen etwa 200 µm und etwa 500 µm hat.

3. Transparenter oder im wesentlichen transparenter Diamantfilm gemäß Anspruch 1 oder Anspruch 2, worin der Diamantfilm im wesentlichen vertikale säulenförmige Diamantkristalle umfaßt, die eine bevorzugte [110]-Orientierung senkrecht zur Basis des Films haben.

4. Im wesentlichen transparenter Diamantfilm gemäß einem vorhergehenden Anspruch, der bis zu 10.000 ppm chemisch kombinierten Wasserstoff aufweist.

5. Im wesentlichen transparenter Diamantfilm gemäß einem vorhergehenden Anspruch, der Diamant-Korngrenzen aufweist, die die säulenförmigen Diamantkristalle trennen, wobei die Grenzen eine Orientierung zwischen 70° und 90° zur Basis des Films haben.

6. Verfahren zum Züchten eines nicht haftenden, im wesentlichen transparenten polykristallinen Diamantfilms auf einem Substrat, umfassend das Hindurchführen einer Wasserstoff-Methan-Mischung

durch eine erhitzte Zone bei einer Temperatur von etwa 600°C bis etwa 1.000°C bei einem Druck von etwa 400 bis 3.199 Pa (3 bis etwa 24 Torr), was zum Erzeugen aktiver Kohlenstoff-Wasserstoff-Arten in der erhitzten Zone genügt, die in einem Abstand von etwa 0,3 bis etwa 1 cm auf der Oberfläche des Substrates aufrechterhalten wird, wobei die in die erhitzte Zone eingeführte Wasserstoff-Methan-Mischung von etwa 1,5 bis etwa 2 Vol.-% Methan, bezogen auf das Gesamtvolumen von Wasserstoff und Methan, aufweist.

7. Verfahren nach Anspruch 6, worin das Substrat ein Molybdän-Substrat ist.

Revendications

1. Film de diamant polycristallin, transparent ou pratiquement transparent, ayant une épaisseur d'au moins environ 50 µm (micromètres).

2. Film de diamant transparent ou pratiquement transparent selon la revendication 1, dont l'épaisseur est comprise entre environ 200 µm (micromètres) et environ 500 µm (micromètres).

3. Film de diamant transparent ou pratiquement transparent selon la revendication 1 ou 2, qui comprend des cristaux de diamant en forme de colonne pratiquement verticale, ayant une orientation [110] préférée perpendiculaire à la base du film.

4. Film de diamant pratiquement transparent selon l'une quelconque des revendications précédentes, qui contient jusqu'à 10.000 ppm d'hydrogène chimiquement combiné.

5. Film de diamant pratiquement transparent selon l'une quelconque des revendications précédentes, qui présente des joints de grains de diamant séparant les cristaux de diamant en forme de colonne, lesdits joints ayant une orientation faisant un angle de 70° à 90° avec la base du film.

6. Procédé pour faire croître sur un support un film de diamant polycristallin, pratiquement transparent, non adhérent, qui comprend l'étape consistant à faire traverser par un mélange d'hydrogène et de méthane, à une pression d'environ 400 à environ 3199 Pa (environ 3 à environ 24 torrs), une zone chauffée à une température d'environ 600 °C à environ 1000 °C, ce qui est suffisant pour produire des espèces carbone-hydrogène actives dans la zone chauffée qui est maintenue à une distance d'environ 0,3 à environ 1 centimètre de la surface du support, le mélange d'hydrogène et de méthane introduit dans la zone chauffée contenant environ 1,5 à environ 2 % en volume de méthane par rapport au volume total d'hydrogène et de méthane.

7. Procédé selon la revendication 6, dans lequel le support est un support en molybdène.

FIG. 1

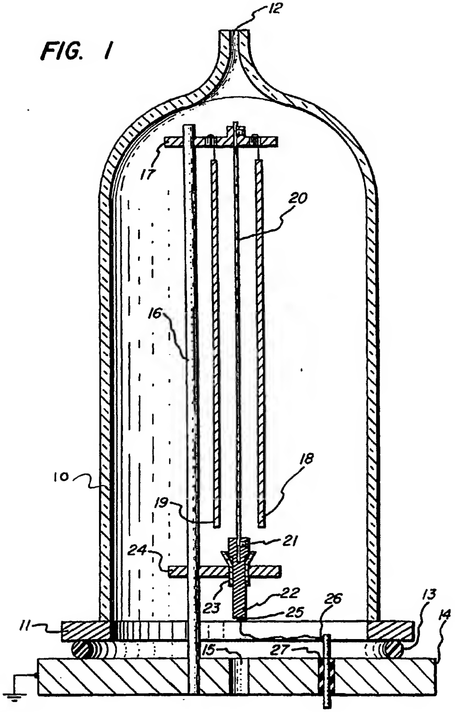
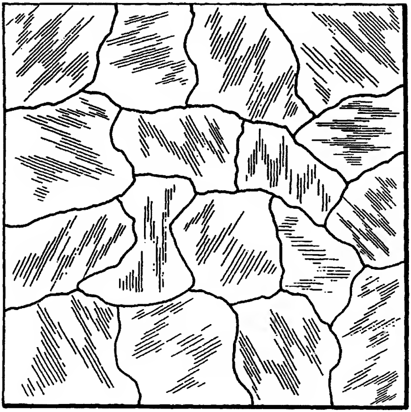


FIG. 2



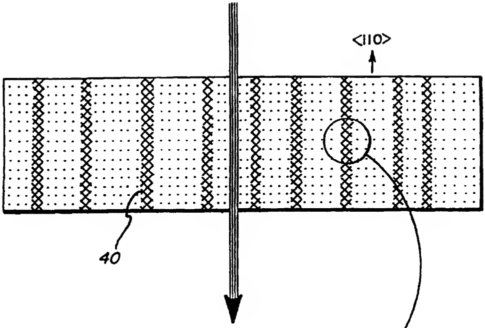


FIG. 3

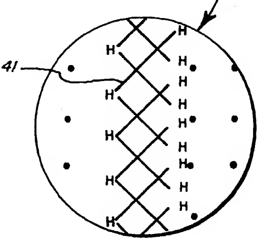


FIG. 3A